# INTERNATIONAL STANDARD ISO 3012

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

# Aviation turbine fuels — Determination of mercaptan sulphur — Amperometric and potentiometric methods

*Carburants aviation pour turbines — Dosage du soufre sous forme de mercaptans — Méthodes ampérométrique et potentiométrique*

**First edition — 1974-06-01**



**UDC 665.743.3 : 546.22 : 545.37** **Ref. No. ISO 3012-1974 (E)**

**Descriptors** : petroleum products, aviation fuels, chemical analysis, determination of content, thiols, amperometric analysis, potentiometric analysis.

Price based on 6 pages

## FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3012 was drawn up by Technical Committee ISO/TC 28, *Petroleum products*, and circulated to the Member Bodies in March 1973.

It has been approved by the Member Bodies of the following countries :

| | | |
|---|---|---|
| Australia | India | South Africa, Rep. of |
| Belgium | Iran | Spain |
| Brazil | Israel | Sweden |
| Bulgaria | Mexico | Thailand |
| Canada | Netherlands | Turkey |
| Chile | New Zealand | United Kingdom |
| Czechoslovakia | Norway | U.S.A. |
| France | Poland | U.S.S.R. |
| Germany | Portugal | |
| Hungary | Romania | |

No Member Body expressed disapproval of the document.





Printed in Switzerland

# Aviation turbine fuels — Determination of mercaptan sulphur — Amperometric and potentiometric methods

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies two methods for the determination of mercaptan sulphur in aviation turbine fuels containing from 0,000 3 to 0,01 % (*m/m*) of mercaptan sulphur. Organic sulphur compounds such as sulphides, disulphides, and thiophene do not interfere. Elemental sulphur in amounts less than 0,000 5 % (*m/m*) does not interfere. Hydrogen sulphide will interfere, if not removed as described in 3.4.1.

## 2 PRINCIPLE

**2.1** The sample is washed with an aqueous solution of acid cadmium sulphate to remove hydrogen sulphide. The determination of mercaptan sulphur in the hydrogen sulphide-free sample is finished either amperometrically or potentiometrically.

**2.2** Using the amperometric finish, the hydrogen sulphide-free sample is dissolved in titration solvent and is titrated amperometrically with silver nitrate standard solution, using a rotating platinum wire indicator electrode and a calomel reference electrode. The diffusion current is measured and plotted against the volume of silver nitrate added. The volume of silver nitrate equivalent to the mercaptan sulphur is determined from the titration curve.

**2.3** Using the potentiometric finish, the hydrogen sulphide free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate standard alcoholic solution, using as an indicator the potential between a glass reference electrode and a silver/silver sulphide indicating electrode. Under these conditions the mercaptan sulphur is precipitated as silver mercaptide and the end point of the titration is shown by a large change in cell potential.

## 3 AMPEROMETRIC METHOD

### 3.1 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to recognized standards for reagent chemicals. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equivalent purity.

**3.1.1 Acetone**

**3.1.2 Sulphuric acid** (1 + 5).

Carefully add 1 volume of concentrated sulphuric acid ($H_2SO_4$, $\rho$ 1,84 g/ml) to 5 volumes of water.

**3.1.3 Supporting electrolyte**

Dissolve 20 g of ammonium nitrate ($NH_4NO_3$) in 100 ml of concentrated ammonium hydroxide ($NH_4OH$, $\rho$ 0,90 g/ml).

**3.1.4 Cadmium sulphate**, acid solution (150 g/l).

Dissolve 150 g of cadmium sulphate ($3CdSO_4.8H_2O$) in water. Add 10 ml of sulphuric acid (3.1.2) and dilute to 1 l with water.

**3.1.5 Potassium chloride**, saturated solution.

Prepare a saturated solution of potassium chloride (KCl) in water.

**3.1.6 Silver nitrate**, 0,100 0 N standard solution.

Dissolve 16,989 g of dry (1 h at 110 °C) silver nitrate ($AgNO_3$) in water and dilute to 1 l with water in a volumetric flask.

**3.1.7 Silver nitrate**, 0,010 0 N standard solution.

Dilute 100 ml of the silver nitrate standard solution (3.1.6) to 1 l with water in a volumetric flask.

### 3.2 APPARATUS

Typical apparatus may be assembled as shown in figure 1, using soldered connections wherever practicable in the electrical circuit.

**3.2.1 Burette**, capacity 25 ml, graduated in 0,1 ml divisions.

NOTE — Burettes of 25 ml capacity conforming to the requirements of ISO/R 385 — Class B are suitable.

**3.2.2 Calomel electrode**, sleeve type pencil electrode, either conventional or double junction type.

**3.2.3 Electrical circuit** as shown in figure 1.

**3.2.4 Microammeter**, d.c. type having a range from 0 to 30 $\mu$A, a sensitivity of 0,2 $\mu$A per division, and an internal resistance of 150 to 500 $\Omega$.

**3.2.5 Rotating electrode**, constructed as follows :

Seal a platinum wire 0,5 to 1,0 mm in diameter and 6 to 8 mm long into the end of soft glass tube, 6 mm outside diameter, that has been shaped into a stirrer blade. Place a few drops of mercury in the glass tube, and make electrical contact between the mercury and the chuck of the stirring motor with a piece of copper wire.

Alternatively, a stationary platinum electrode may be used provided the solution is stirred at a constant speed.

**3.2.6 Stirrer**, that can maintain a constant speed in the range from 500 to 1 000 rev/min. The stirrer may be so constructed that an electrical connection can be made between the rotating electrode and the potential divider.

**3.2.7 Voltmeter**, d.c. type having a range of 0 to 1 V with a sensitivity of 0,01 V per division.

### 3.3 PREPARATION OF APPARATUS

**3.3.1** Remove the rubber stopper from the side opening of the calomel electrode (3.2.2), or lower the rubber sleeve, and lower the glass sleeve for a few seconds to allow the potassium chloride electrolyte to wet the ground glass joint.

**3.3.2** Place 100 ml of acetone (3.1.1) and 5 ml of the supporting electrolyte solution (3.1.3) in a 300 ml tall-form beaker. Place the beaker on the titrating stand and adjust its position so that the tips of the electrodes are at least 25 mm below the surface of the liquid. Start the rotating electrode stirring motor and adjust its speed so that it is



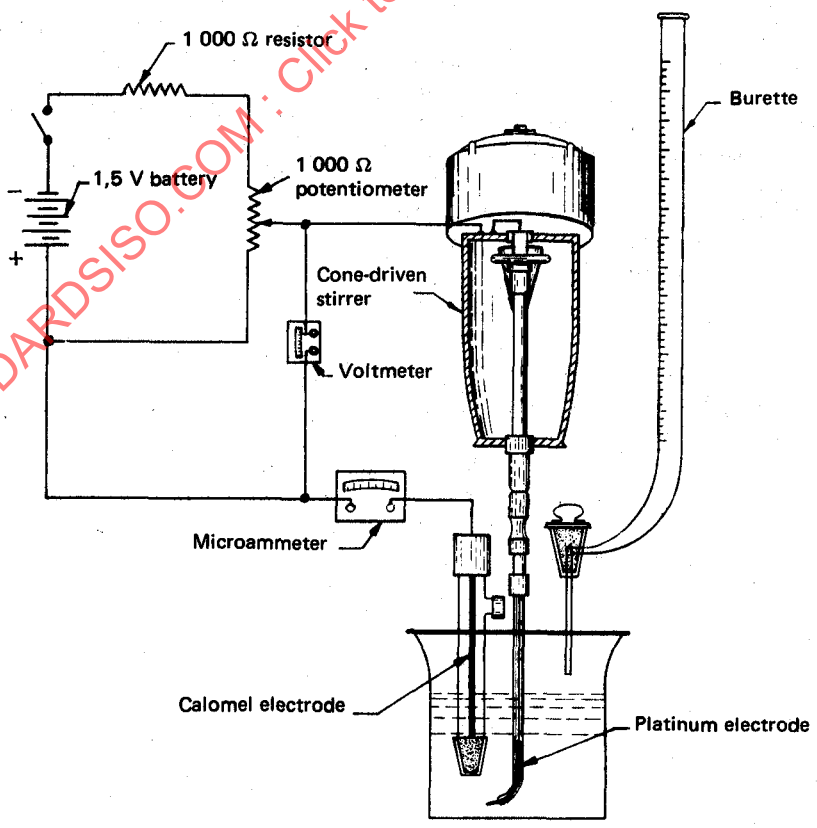


FIGURE 1 — **Diagram of amperometric titration apparatus**

within the range of 500 to 1 000 rev/min. During a titration this speed must be maintained constant. Close the electrical circuit (3.2.3) and adjust the potential divider so that $-0,25 \pm 0,02$ V is applied to the platinum electrode, as indicated by the voltmeter (3.2.7). Once the correct voltage has been obtained, do not change the setting of the potential divider during a determination.

**3.3.3** Check the apparatus by making a trial titration as follows : Record the microammeter reading (see note). Add 0,10 ml of silver nitrate standard solution (3.1.7) and record the burette and microammeter readings. Continue in this manner, adding small increments of silver nitrate standard solution until a total of 1,00 ml has been added. Plot, on linear graph paper, the quantity in millilitres of silver nitrate standard solution used against the corresponding reading in microamperes. Draw a straight line through the plotted points. The intersection of this line with a horizontal line drawn through the microammeter reading at 0 ml of silver nitrate standard solution indicates the volume of silver nitrate standard solution used to reach the end point. This volume should be less than 0,05 ml of silver nitrate standard solution. If most of the points fall on a reasonably straight line, consider the apparatus to be in satisfactory working condition.

NOTE — The current may increase to 20 or 30 $\mu$A at first, but it will decrease to zero or slightly above in a few minutes.

## 3.4 PROCEDURE

### 3.4.1 Removal of hydrogen sulphide

Test the sample qualitatively for hydrogen sulphide ($H_2S$) by shaking 5 ml of the sample with 5 ml of the cadmium sulphate acid solution (3.1.4). If no precipitate appears, proceed with the analysis of the sample as described in 3.4.2. If a yellow precipitate appears, remove the hydrogen sulphide in the following manner : Place a quantity of the sample, three to four times that required for the analysis, in a separating funnel containing a volume of the cadmium sulphate acid solution equal to one half that of the sample and shake vigorously. Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with another portion of the cadmium sulphate acid solution. Again draw off the aqueous phase, and wash the sample with three 25 to 30 ml portions of water, withdrawing the water after each washing. Filter the hydrocarbon through a rapid filter paper. Test a small portion of the washed sample in a test tube with a few millilitres of the cadmium sulphate acid solution. If no further precipitate is formed, proceed as directed in 3.4.2. If a precipitate appears, repeat the extraction with the cadmium sulphate acid solution until all the hydrogen sulphide has been removed.

### 3.4.2 Analysis of sample

Measure with a pipette (see note 1), or weigh, 20 to 50 ml of the original or hydrogen sulphide-free sample prepared as described in 3.4.1 into a 300 ml tall-form beaker containing 100 ml of acetone and 5 ml of the supporting electrolyte (see note). Place the beaker on the titration stand, start the stirring motor, and close the electrical circuit. Begin the titration by adding small increments of the silver nitrate standard solution (3.1.7). Record the microammeter and burette readings after each addition. The end point region is indicated by a rapid increase in the microammeter readings. When the microammeter indicates that the end point has been passed, add four or five small increments of silver nitrate standard solution, recording the microammeter and burette readings after each addition. Plot the cumulative volume of silver nitrate standard solution used against the corresponding readings in microamperes on linear graph paper. Draw a straight line through the increasing current readings and a horizontal line through the minimum current readings (see figure 2). The point of intersection of the two lines indicates the volume of silver nitrate standard solution that is equivalent to the mercaptan sulphur content of the sample.

NOTES

1 If the test portion is measured volumetrically, the density shall be determined by a suitable method capable of reproducing results to within 0,001 5 g/ml.

2 A larger amount of acetone may be used if it is required to dissolve the sample.

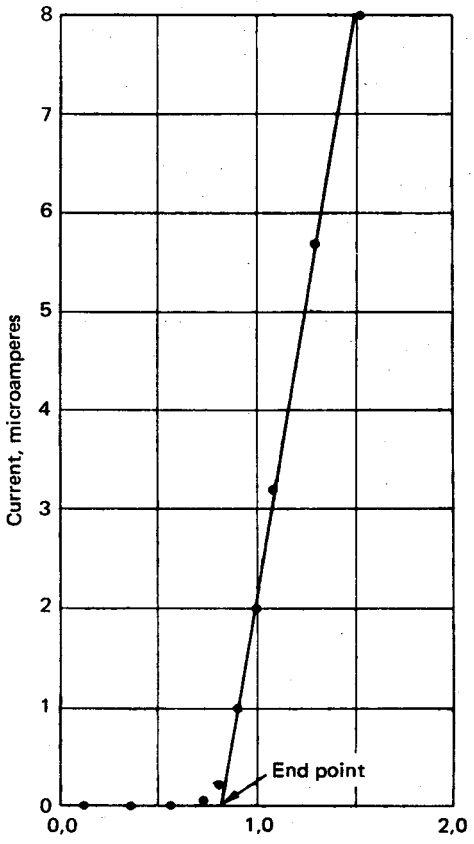


FIGURE 2 — **Typical amperometric titration curve for liquid hydrocarbon samples**

### 3.5 CALCULATION

The mercaptan sulphur content, as a percentage by mass, of the sample is given by the formula

$$3{,}206\,\frac{VT}{m}$$

where

$V$ is the volume, in millilitres, of silver nitrate solution required;

$T$ is the normality of the silver nitrate solution;

$m$ is the mass, in grams, of the test portion.

### 3.6 PRECISION

The following criteria shall be used for judging the acceptability of results (95 % confidence level).

**3.6.1** Duplicate results by the same operator shall be considered suspect if they differ by more than the following amounts :

| Mercaptan sulphur content % (*m/m*) | Repeatability |
|---|---|
| 0,000 3 to 0,001 | 0,000 1 |
| 0,001 to 0,005 | 0,000 2 |
| 0,005 to 0,010 | 0,000 5 |

**3.6.2** The results submitted by each of two laboratories shall be considered suspect if the two results differ by more than the following amounts :

| Mercaptan sulphur content % (*m/m*) | Reproducibility |
|---|---|
| 0,000 3 to 0,001 | 0,000 4 |
| 0,001 to 0,005 | 0,000 6 |
| 0,005 to 0,010 | 0,000 9 |

## 4 POTENTIOMETRIC METHOD

### 4.1 REAGENTS[1)]

**4.1.1 Cadmium sulphate**, acid solution (150 g/l).

See 3.1.4.

**4.1.2 Sodium sulphide** solution (10 g/l).

Dissolve 10 g of sodium sulphide ($Na_2S$) in water and dilute to 1 l with water. Prepare a fresh solution as needed.

**4.1.3 Titration solvent.**

Dissolve 2,7 g of sodium acetate trihydrate ($NaC_2H_3O_2.3H_2O$), or 1,6 g of anhydrous sodium acetate ($NaC_2H_3O_2$) in 20 ml of oxygen-free water, pour into 975 ml of *iso*propyl alcohol (99 %) (see note to 4.1.6) and add 4,6 ml of glacial acetic acid. To remove dissolved oxygen purge the solution with a rapid stream of nitrogen for 10 to 15 min each day prior to use; keep protected from the atmosphere.

**4.1.4 Potassium iodide**, 0,1 N standard solution.

Dissolve approximately 17 g of potassium iodide (KI), weighed to the nearest 0,01 g, in water and dilute to 1 l in a volumetric flask with water. Calculate the exact normality.

**4.1.5 Silver nitrate**, 0,1 N standard alcoholic solution.

Dissolve 17 g of silver nitrate ($AgNO_3$) in 100 ml of water and dilute to 1 l with *iso*propyl alcohol (99 %) (see note to 4.1.6), store in a dark bottle and standardize weekly.

To standardize, add 6 drops of concentrated nitric acid ($HNO_3$, $\rho$ 1,42 g/ml) to 100 ml of water in a 300 ml tall-form beaker, and remove the oxides of nitrogen by boiling for 5 min. Cool, pipette 5 ml of the potassium iodide solution (4.1.4) into the beaker, and titrate with the silver nitrate solution, choosing the end point at the inflection of the titration curve.

**4.1.6 Silver nitrate**, 0,01 N standard alcoholic solution.

Prepare daily by dilution of 100 ml of silver nitrate alcoholic solution (4.1.5) to 1 l with *iso*propyl alcohol (99 %) in a volumetric flask. Calculate the exact normality.

NOTE – It is important to pass the *iso*propyl alcohol through a column of activated alumina to remove peroxides that may have formed on storage; failure to remove peroxides will lead to low results.

### 4.2 APPARATUS

**4.2.1 Burette**, capacity 10 ml, graduated in 0,05 ml intervals, with a tip that extends approximately 120 mm below the stopcock.

NOTE – Burettes of 10 ml capacity conforming to the requirements of ISO/R 385 – Class B are suitable.

1) For purity of reagents, see 3.1.